

APPLICATION

FOR

UNITED STATES LETTERS PATENT

FOR

MEDIATED ELECTROCHEMICAL OXIDATION OF
BIOLOGICAL WASTE MATERIALS

BY

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Mediated Electrochemical Oxidation of
Biological Waste Materials

This application claims the benefit of 60/145,972, filed 7-29-99.
FIELD OF THE INVENTION

This invention relates generally to a process and apparatus for the disposal of biological waste which includes, but is not limited to, medical waste, infectious waste, pathological waste, animal waste, and sanitary waste and henceforth referred to as biological waste.

BACKGROUND OF THE INVENTION

The cost of disposing of biological waste in the U.S. is more than \$5 billion per year. The capital cost of the equipment required is in the hundreds of millions of dollars. All institutions and businesses that generate and handle this category of waste have needs to provide safe effective and inexpensive disposal of the waste. In recent years there has been increasing concern over the disposal of biological waste. The two principal methodologies for the disposal of this waste are incineration and dumping in landfills.

The Environmental Protection Agency (EPA) has issued new regulations that require incinerators to reduce their emissions to very stringent levels for products that are exhausted from biological waste incinerators. The new regulations will, for practical purposes, close down or require major modifications to almost all such incinerators by the year 2001. Municipal landfills have already begun to refuse to accept biological waste especially if it is identifiable as medical waste. Most alternatives to these two methods involve thermal methods that emit products into the atmosphere that are not acceptable.

Biological waste is defined as any waste that is considered by any of, but not limited to, the following statutes and regulations:

- * New Jersey State Statute, "Comprehensive Regulatory Medical Waste Management Act", P.L. 1989, c. 34 (C.13.1E-48.13).
- * New York State Environmental Conservation Law, TITLE 15, "STORAGE, TREATMENT, DISPOSAL AND TRANSPORTATION OF REGULATED MEDICAL WASTE", Section 27-1501. Definitions.
- * New York State Public Health Law, TITLE XIII, "STORAGE, TREATMENT AND DISPOSAL OF REGULATED MEDICAL WASTE", Section 1389-aa. Definitions.
- * CALIFORNIA HEALTH AND SAFETY CODE, SECTION 117635. "Biohazardous Waste" Title 25 Health Services, Part I.
- * Texas Department of Health, Chapter 1 Texas Board of Health, "Definition, Treatment, and Disposition of Special Waste from Health Care-Related Facilities, Section 1.132 Definitions.
- * 40 C.F.R. 60.51(c) PROTECTION OF ENVIRONMENT; Standards of performance for new stationary sources.
- * 40 C.F.R. 240.101 PROTECTION OF ENVIRONMENT; Guidelines for the thermal processing of solid wastes (Section P only).
- * 49 C.F.R. 173.134 TRANSPORTATION; Class 6, Division 6.2- Definitions, exceptions and packing group assignments.
- * 33 C.F.R. 151.05 TITLE 33--"NAVIGATION AND NAVIGABLE WATERS; VESSELS CARRYING OIL, NOXIOUS LIQUID SUBSTANCES, GARBAGE, MUNICIPAL OR COMMERCIAL WASTE, AND BALLAST WATER"; Definitions (medical waste only).

Biological waste is a relatively new problem for today's technological society. The definition of this waste has been expanding in its coverage of materials that must be handled in a controlled manner. The foregoing list of state statutes and United States federal

regulations are overlapping but necessary to accurately define the materials because no single statute or regulation covers all the materials to which this invention applies.

Mediated Electrochemical Oxidation (MEO) processes represent a mature science in the industrial complex over the past two decades. The orientation to date has been focused on the dissolution of transuranic metals and destruction of organics in mixed waste from the chemical reprocessing of irradiated nuclear reactor fuel, and controlled oxidation and destruction of organic-based military munitions and organophosphorus chemical weapon nerve agents, as is represented by patents dating back into the mid-eighties.

Research into the application of the MEO process to date has involved the use of the process to dispose of materials in these areas. In the first area, the MEO uses an electrochemical cell in which the electrolyte is generally restricted to a composition of nitric acid and silver ions. The silver ion serves as the regenerable mediating oxidizing species which is used in a oxidative dissolution of plutonium dioxide to recover plutonium contained in solid waste from processes, technological and laboratory waste (U.S. Patent 4,749,519), and subsequently extended to the dissolution of the plutonium dioxide component of mixed oxide fuel (coprecipitated uranium and plutonium oxide) (U.S. Patent 5,745,835).

In the second area, the MEO process was used: (a) for the decomposition (i.e. oxidation) of organic matter contained in the mixed solid waste generated in extracting plutonium from irradiated nuclear reactor fuel (U.S. Patents 4,874,485; 4,925,643); (b) controlled oxidation of organic military munitions (U.S. Patent 5,810,995); and (c)

destruction of organophosphorus nerve agents (U.S. Patent 5,855,763).

Both of the two areas discussed have involved similar use of the MEO process using nitric acid and silver ions being generated by an electrochemical cell with the anode and cathode being separated by a membrane. The two uses have differed in the temperature range used in each of the applications. The second use is operated between 50°C and slightly below 100°C to take advantage of the generation of the secondary oxidation species to assist in oxidizing organic materials. The first use is operated below 50°C (generally around 25°C or room temperature) to minimize Ag(II)- water reactions because unlike the Ag(II) ion, not all of the secondary oxidizing species have an oxidation potential sufficient to oxidize plutonium dioxide to a soluble species.

Others have substituted cerium and nitric acid, cobalt and nitric acid, and cobalt and sulfuric acid for the silver and nitric acid as the electrolyte (U.S. Patents 5,516,972; 5,756,874). The temperatures vary among the three electrolytes being substituted for the silver and nitric acid combination. Most recently, ruthenium in a nearly neutral solution has been proposed as the electrolyte in a MEO process to decompose organic materials, which would operate between 50°C and 90°C (*Platinum Review*, Jul 1998). All of the descriptions reviewed are similar in their application to the decomposition of organic materials and differ in their choice of electrolyte(s), pH, concentrations, and the operating temperature range over which they are applied.

These and other objects and features of the invention are apparent in the disclosure, which includes the above and ongoing written specification, with the drawings.

SUMMARY OF THE INVENTION

The invention relates to a method and apparatus for the mediated electrochemical oxidation (MEO) of wastes, such as biological materials and has particular application to, but is not limited to, biological waste, medical waste, infectious waste, pathological waste, animal waste, and sanitary waste (henceforth collectively referred to as biological waste).

A mediated electrochemical oxidation process involves an oxidizing electrolyte, wherein at least one oxidizing species is electrochemically generated in an electrochemical cell. A membrane in the electrochemical cell separates the anolyte and catholyte. The preferred MEO process uses as mediator ions, for example, the following metals: Ag, Ce, Co, Fe, Mn or Ru in nitric acid, sulfuric acid or phosphoric acid as the anolyte. A cost reduction can be achieved in the a basic MEO process by using anions that are useable in alkaline solutions such as NaOH and KOH, since the oxidation potentials usually decrease with increasing pH. The catholyte may contain the same acid as the anolyte, but not necessarily in the same concentration. The process operates over the temperature range from room temperature up to a temperature slightly below the boiling point of the electrolyte solution (usually the temperature will be below 100°C) during the destruction of the biological waste.

The MEO process begins with the electrochemical oxidation of the dissolved mediator ions to one of their higher valence states, after which these ions oxidize the biological waste and are themselves reduced

down to their initial lower valence state, whereupon they are again electrochemically oxidized back up to their higher valence state. In the case of some higher valence oxidized species, a second oxidation process is possible.

At higher temperatures (i.e., above about 50°C) these higher valence oxidizer species react with the aqueous solution to produce a variety of powerful oxidizing free radicals (e.g., •OH, etc.) and hydrogen peroxide, etc. Decomposition of the hydrogen peroxide into free hydroxyl radicals is well known to be promoted by ultraviolet irradiation. The MEO process biological waste destruction rate using these species, therefore, will be increased by ultraviolet irradiation of the reaction chamber anolyte.

The principals of the oxidation process in which the hydroxyl free radical cleaves chemical bonds and oxidizes organic compounds have been widely documented, resulting in the formation of successively smaller chained hydrocarbon compounds. The intermediate compounds formed are easily oxidized to carbon dioxide and water during sequential reactions.

One distinction between the prior art and this invention is in the application to biological waste, which distinctly differs from all prior applications. The prior art processes and their supporting patents may focus on organic materials, but they clearly distinguish from biological waste both in describing their processes and specifically in the examples of materials being treated by their processes. The materials are generally characterized as complex organic molecules associated with industrial processes. The prior art does not describe or refer to a single process that is biological in nature. Prior art processes that specifically deal with biological waste do not use the MEO process to

dispose of those categories of waste.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic representation of a system for destroying biological waste materials.

Figure 2 is a schematic representation of the preferred embodiment.

Figure 3 is a schematic representation of the steps of the process used in the apparatus.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

MEO Chemistry

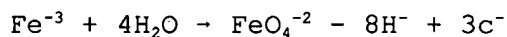
Mediated Electrochemical Oxidation (MEO) process chemistry described in this patent uses one or more of the following metallic ions: silver, cerium, cobalt, iron, manganese and ruthenium in the anolyte as the mediator. The catholyte is composed of one of the following acids; nitric, sulfuric, or phosphoric.

The MEO Apparatus is unique in that it accommodates the numerous choices of mediator metallic ions and acids by draining, flushing, and refilling the system with the electrolyte of choice.

Because of redundancy and similarity in the description of the various metallic ions, only the iron and nitric acid combination is discussed in detail. The Fe(VI) ion (i.e. FeO_4^{2-} species) has an oxidation potential sufficient to react with water to produce secondary oxidation species (e.g., hydroxyl free radicals, etc.). The remainder of this discussion addresses the more complex Fe(VI) process as it not

only addresses the oxidation due to the metal ions but also the secondary oxidation species.

Figure 1 shows an MEO Apparatus in a schematic representation of the system for destroying biological waste. At the anode of the electrochemical cell 17 Fe(III) ions (Fe^{+3} , ferric) are oxidized to Ag Fe(VI) ions (FeO_4^{-2} , ferrate),



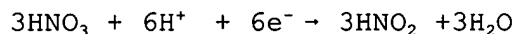
If the anolyte temperate is sufficiently high, typically above 50°C , the Fe(VI) species may undergo a redox reaction with the water in the aqueous anolyte. The oxidation of water proceeds by a sequence of reactions producing a variety of intermediate reaction products, some of which react with each other. A few of these intermediate reaction products are highly reactive free radicals including, but not limited to the hydroxyl ($\bullet\text{OH}$) and hydrogen peroxy ($\bullet\text{HO}_2$) radicals. Additionally, the mediated oxidizer species ions may interact with the stated acid in the anolyte (HNO_3 , H_2SO_4 , or H_3PO_4) to produce free radicals typified by, but not limited to $\bullet\text{NO}_3$. Another possible source of free radicals from the electrolyte acids is the direct oxidation of the NO_3^- , SO_4^{-2} , or PO_4^{-3} ions at the anode of the cell. The population of hydroxyl free radicals may be increased by ultraviolet irradiation of the anolyte in the reaction chamber to cleave the hydrogen peroxide molecules, intermediate reaction products, into two such radicals.

These secondary oxidation species in conjunction with Fe(VI) ions oxidize the biological materials.

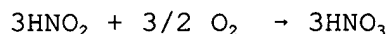
The oxidizers react with the biological waste to produce CO_2 and water. These processes occur in the anolyte on the anode side of the system in the reaction chamber 5. Addition of iron ions to non-iron-

based MEO systems are also proposed as this has the potential for increasing the overall rate of medical waste oxidation compared to the non-iron MEO system alone. The electrochemical oxidation proceeds much faster for iron ions than for most other mediator ions. Therefore, if the two step process of electrochemically forming an FeO_4^{-2} ion and the FeO_4^{-2} ion oxidizing the mediator ion to its higher valence occurs faster than the direct electrochemical oxidation of the mediator ion, then there is an overall increase in the rate of biological waste destruction.

Membrane M separates the anode and the cathode chambers in the electrochemical cell. Hydrogen ions (H^+) travel through the membrane M due to the electrical potential from the power supply 21 applied between the electrodes 18 and 19. In the catholyte the nitric acid is reduced to nitrous acid



by the reaction between the H^+ ions and the nitric acid. Oxygen is introduced into the catholyte through the air sparge 35, and the nitric acid is regenerated,



The overall process results in the biological waste being converted to carbon dioxide, water, and a small amount of inorganic compounds in solution or as a precipitate.

The biological waste may be a liquid, solid, or a mixture of solids and liquids. The biological waste is introduced into the top of biological waste basket 3 in the reaction chamber 7. The apparatus continuously circulates the anolyte portion of the electrolyte through the reaction chamber to promote maximum contact area between the waste

and the oxidizing species. Contact of the oxidizing species with incomplete oxidation products that are gaseous at the conditions within the reaction chamber 5 may be enhanced by using conventional techniques for promoting gas/liquid contact 7 (e.g., ultrasonic vibration, mechanical mixing). All surfaces of the apparatus in contact with the anolyte or catholyte are composed of stainless steel or nonreactive polymers such as PTFE (Teflon™).

The anolyte circulation system contains a pump 9 and a removal and treatment system 12 (e.g., filter, centrifuge, hydrocyclone, settling tank, etc.) to remove any precipitate or other insoluble inorganic compounds that form as a result of mediator ions (e.g., Ag, Ce, Co, Fe, Mn, Ru) reacting with the small amount of chlorine (or other anions) that may be present in the waste stream. The anolyte is returned to the electrochemical cell 17, which completes the circulation in the anode side (A).

Waste may be added to the basket 3 in the reaction chamber either continuously or in the batch mode. The anolyte starts either at the operating temperature or at a lower temperature, which subsequently is increased by the thermal control 7 to the desired operating temperature for the specific waste stream. Waste may also be introduced into the apparatus, with the concentration of electrochemically generated oxidizing species in the anolyte being limited to some predetermined value between zero and the maximum desired operating concentration for the waste stream by control of the electric current by the system power supply 23 supplied to the electrochemical cell 17. The electrolyte is composed of an aqueous solution of mediator ions and acid (nitric, phosphoric, or sulfuric acid) and is operated over the temperature range

from room temperature to slightly below the boiling point of the electrolytic solution (usually less than 100°C).

Considerable attention has been paid to halogens and their interactions with silver ions, which are of much less importance to this invention. The biological waste contains relatively small amounts of these halogen elements compared to the halogenated solvents and nerve agents addressed in the cited patents. Silver ions are required to oxidize those organic compounds in the cited patents while in this patent there is a choice of mediator ions. The choice of mediator ions effects the cost of the electrolyte and may be used to avoid formation of insoluble inorganic compounds thereby preventing removal of the mediator.

The residue of the inorganic compounds is flushed out of the treatment system 12 during periodic maintenance if necessary. If desired inorganic compounds may be recovered from the process stream using any one of several chemical or electrochemical processes. The apparatus operates across the temperature range from room temperature to slightly below the boiling point of the electrolyte (generally below 100°C) adjusted to the composition of the materials introduced in to the reaction chamber. The system is monitored for the production of CO₂ as a means of determining when the decomposition process is complete.

The entireties of US Patents 4,749,519; 4,874,485; 4,925,643; 5,745,935; 5,810,995; and 5,855,763 are included herein by reference for their relevant teachings.

MEO Apparatus

A schematic drawing of the MEO apparatus shown in Figure 1

illustrates the application of the MEO process to the destruction of biological waste. The lid 1 is raised and the biological waste is placed or poured into the basket 3 in the reaction chamber 5 as liquid, solid, or a mixture of liquids and solids. A small thermal control unit is connected to the reaction chamber 5 to heat or cool the anolyte to the selected temperature range.

The anolyte portion of the electrolyte solution contains mediated oxidizer species and secondary oxidizing species. The anolyte is circulated into the reaction chamber from the electrochemical cell 17 by pump 9. The anolyte portion and catholyte portion of the electrolyte are separated by a membrane M in the electrochemical cell 17. The electrochemical cell 17 is powered by a DC power supply 21 typically delivering 2 to 6 volts. The DC power supply 21 operates off a typical 110 volt or 220 volt AC line.

The electrolyte containment boundary is composed of materials resistant to the oxidizing electrolyte (e.g., stainless steel, PTFE, PTFE lined stainless steel, etc.). Reaction products resulting from the oxidizing processes being conducted on the anolyte side (A) of the system that are gaseous at the anolyte operating temperature and pressure are discharged to the condenser 15. The more easily condensed products of incomplete oxidation are separated from the off gas stream 16 and are returned to the anolyte reaction chamber for further oxidation. The noncondensable incomplete oxidation products (e.g., low molecular weight organics, carbon monoxide, etc.) are reduced to acceptable levels for atmospheric release by a gas cleaning system 15.

Various scrubber/absorption columns are used or the gas mixture is recontacted with the anolyte to provide adequate reaction time and

contact area to ensure the required degree of oxidation, if necessary. A major product of the oxidation process is CO_2 , which is vented 16 out of the system. An optional inorganic compound removal and treatment systems 13 is used should there be more than trace amount of chlorine, or other precipitate forming anions present in the biological waste being processed.

A pump 39 circulates the catholyte portion of the electrolyte through the portion of the electrochemical cell 17 on the cathode side of the membrane. The catholyte portion of the electrolyte flows into a catholyte reservoir 25. A small thermal control unit 31 is connected to the catholyte reservoir 25 to heat or cool the catholyte to the selected temperature range. External air is introduced through an air sparge 35 into the catholyte reservoir 25. The oxygen contained in the air oxidizes nitric acid and the small amounts of nitrogen oxides produced by the cathode reactions to nitric acid and NO_2 , respectively. Contact of the oxidizing gas with nitrous acid may be enhanced by using conventional techniques for promoting gas/liquid contact by a mixer 33 (e.g., ultrasonic vibration, mechanical mixing, etc.). Systems using non-nitric acid catholytes may also require air sparging to dilute and remove off gas such as hydrogen. An off gas cleaning system 36 is used to remove any unwanted gas products (e.g. NO_2 , etc.). The cleaned gas stream, combined with the unreacted components of the air introduced into the system is discharged through the off gas vent 37. Optional mediated oxidizer species recovery (i.e. metallic ions) and treatment system 20 is positioned on the catholyte side. Some mediated oxidizer species may cross the membrane M in small amounts, and this option is available if it is necessary to recover the species (i.e. metallic

ions).

In a preferred embodiment shown in Figure 2, System Model 1.0 is sized for use in a medical office or laboratory. Other systems are similar in nature but are scaled up in size to handle a larger capacity of waste, such as patient's room, operating room, laboratories, etc.

The system has a control keyboard 8 for input of commands and data. There is a monitor screen to display the systems operation and functions. Below these controls are the status lights 6 for on, off, and standby. Hinged lid 1 is opened and the biological waste is deposited in the basket 3 in the chamber 7. A lid stop 2 keeps the lid opening controlled. In the chamber is the aqueous acid and mediated oxidizer species solution in which higher valence oxidizer species initially may be present or may be generated electrochemically after introduction of the waste and application of power 23 to the cell 17. Power supply 21 provides direct current to an electrochemical cell 17. Pump 9 circulates the anolyte portion of the electrolyte and the biological waste material is rapidly oxidized at room temperature and ambient pressure. The oxidation process will continue to break the materials down into less and less complex molecules until they reach CO₂, water, and some trace inorganic salts. Any residue is passified in the form of a salt and may be periodically removed through the flush and drain outlets 11. The electrolyte may be changed through this same plumbing. The catholyte reservoir has two flange joints 27 and 29, which allow access to the reservoir for cleaning.

Due to low power consumption and low consumption of mediated oxidizer species and electrolyte acid the device may remain activated throughout the day, and biological waste may be added as it is

generated. The compactness of the device makes it ideal for offices and surgeries as well as suitable for use with high volume inputs of laboratories and hospitals. The process operates at low temperature and ambient atmospheric pressure and does not generate toxic compounds during the destruction of the biological waste, making the process indoor compatible. The system is scalable to a unit large enough to replace a hospital incinerator system. The CO₂ oxidation product is vented out the wall vent 16, and the atmospheric air vent 37 for the cathode side is shown.

Steps of the Operation of the MEO Process

Figure 3 is a schematic of the steps in the operation of process of destroying biological waste in the System Model 1.0. The system is started 43 by engaging the "On" button on the control keyboard 8. The monitor screen 10 displays the steps of the process in the proper sequence. The lid 1 is opened and the biological waste is placed 45 in the basket. The thermal controls 7 and 31 are turned on 47/61, which brings the electrolyte in to the temperature range for proper function. The electrochemical cell is energized 49,63. The pumps 9 and 39 begin to circulate 51,65 the anolyte and catholyte respectively.

As soon as the electrolyte circulation is flowing throughout the system, the mixers begin to operate 53 and 67. The biological waste is being decomposed into water and CO₂, which is discharged 55 out of the CO₂ vent 16. Air is drawn 69 into the catholyte reservoir 25, and excess air is discharged 70 out the atmospheric vent 37. When the CO₂ production ceases, the biological waste has been fully destroyed 57, and the system goes to standby 59.

Examples

Example (1): The device performance parameters may be estimated for medical/pathological waste by analyzing the electrochemical oxidation of human protoplasm, stated in the literature to consist of 67 weight % water, 29 weight % organic solids and 4 weight % minerals. These organic solids are composed of proteins (15 weight %), lipids (13 weight %) and carbohydrates (1 weight %). For this analysis it is assumed the protein is collagen ($C_{102}H_{149}O_{38}N_{31}$), the lipids, or fats ($C_{57}H_{110}O_6$) and the carbohydrates are glucose units ($C_6H_{12}O_6$), and the oxidation products are H_2O , CO_2 and NO_2 . Assuming a 3-volt cell potential and 100 percent current efficiency, it requires 8.2 kWh to oxidize 1-kg human protoplasm. The time required may be determined by (1) the electrode surface area of the cell (i.e., 0.5 amp/cm² current density limit) and (2) the capacity of the power supply at 3 volts.

Anolyte is in the range of 1 to 22 M nitric acid, typically about 4 to 8M nitric acid, 0.01 to a saturated solution of a soluble iron (ferric) typically 0.5M soluble iron ferric salt (usually but not limited to ferric nitrate). If augmented by the addition of a soluble Ag, Ce, Co, Mn, or Ru salt in the range 0.1 to a saturated solution, the lower limit of the soluble iron salt concentration may be reduced to 0.001 M. Catholyte is in the range of 1 to 22 M nitric acid, typically about 4 to 8M nitric acid. The apparatus is operated between room temperature and slightly below the boiling point. In the alternative acids case the range of 1-19 M sulfuric and phosphoric acids for mediators soluble in them in the same concentration ranges for Fe^{+3} .

Example (2): The MEO process produces CO_2 , water, and trace inorganic salts, all of which are considered benign for introduction

into the environment by regulatory agencies. The cost of using the MEO process in this invention is competitive with both the incineration and landfill methodologies. The MEO process is uniquely suited for destruction of biological waste because water, which constitutes a major portion of this waste (e.g., tissue, body fluids, etc.) is actually a source of secondary oxidizing species rather than parasitic reactions competing for the mediator oxidizer species. Furthermore, the energy that must be provided in the MEO process to heat the waste stream water component from ambient to the electrolyte operating temperature (i.e., 80°C maximum temperature increase) is trivial compared to the water enthalpy increase required in autoclave or incineration based processes.

Example (3): The system is unique relative to earlier art, since it is built to operate in a hospital room or laboratory where it must be compatible with people working in close proximity to the system as well as next to people being treated for medical conditions.

Example (4): The system is built to require limited skill to operate it. The system needs to be accessed during its operating cycle so that more biological waste may be added and needs to remain compatible with the room environment.

Example (5): The system is built to operate with materials that are safe to handle in the environment in which it is to be used. The biological waste contains little or no substances that react with our choice of electrolytes to produce volatile compounds that would offer a problem in the room environment. The system may operate at temperatures less than 100°C and at ambient atmospheric pressure, which adds to the indoor compatibility.

Example (6): The simplicity of the new system built for use with

biological waste produces a system less expensive to operate and cleaner to use than existing waste treatments. The system complexity is reduced by comparison to previous MEO systems, since there is not a requirement to deal with quantities of halogens. The system is truly a 'green machine' in the sense of an environmentally benign system.

Example (7): The system is built so that the composition of the electrolyte may be changed to adapt the system to a selected composition of the biological waste stream.

Example (8): The system flexibility provides for the introduction of more than one metallic ion resulting in marked improvement in the efficiency of the electrolyte. Furthermore, it desensitizes the electrolyte to chlorine ions in solution.

While the invention has been described with reference to specific embodiments, modifications and variations of the invention may be constructed without departing from the scope of the invention.